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(54) Diesel fuel additives and diesel fuel composition

(57) There is provided a diesel fuel additive comprising a salt of a carboxylic acid and an aliphatic amine, or an amide obtained by dehydration-condensation between a carboxylic acid and an aliphatic amine. The fuel additive can be incorporated into a diesel fuel in an amount of not more than 1 wt.%. The additive reduces the amount of deposit in the injection nozzle of a compression-ignition diesel engine, improves lubricity of the diesel fuel, and reduces wear of the fuel injection pump of the engine.

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Description

The present invention relates to a diesel fuel additive and a diesel fuel composition, and particularly to a diesel fuel additive which is effective in reducing an amount of deposit on an injection nozzle of a compression-ignition diesel engine, increasing lubricity of the diesel fuel, and reducing wear of a fuel injection pump in the engine, and a diesel fuel composition containing the diesel fuel additive.

Recently, since much attention has been paid to environmental problems on earth, various countries have pushed forward with the enhancement of regulations on exhaust gas produced by diesel engine cars and reduction of sulfur content of diesel fuel. Most regulations have a target to reduce the sulfur content to less than 0.05 weight % (less than 0.05 mass %). In Japan, the sulfur content of diesel fuel has already been regulated to be less than 0.2 weight %, since October of 1992. As from 1997, the sulfur content shall be regulated to be less than 0.05 weight %.

The reduction of the sulfur content results in reduction of sulphuric acid particulates in exhaust gas of diesel engine cars. It is reported, however, that an amount of emitted products such as particulates are also effected, that is, increased, by formation of deposits on the fuel injection nozzle. Further reported is that deposits on the injection nozzle also causes other adverse problems such as increase of black smoke and decrease of fuel economy. Therefore, it is now required to develop a detergent for injection nozzle, from viewpoints of protection of environment and resource.

The reduction of sulfur content in diesel fuel goes ahead in the United States of America and European countries. In these countries, it is reported that the reduction of sulfur content may cause abnormal wear of the fuel injection pump, and troublesome engine operations. These problems are considered to be caused by decrease of lubricity of the diesel fuel of low sulfur content. The decrease of lubricity of the diesel fuel is thought to be caused by removal of lubricants of natural origin when the diesel fuel is desulfurized in the hydrogenating desulfurization process.

For the above reasons, it is required to provide an additive which is able to give to the diesel fuel of low sulfur content an anti-wear property and an improved friction property of the same level as that observed in the use of the conventionally employed diesel fuels. The improvement of anti-wear property and friction property is also of value for diesel fuels of not sufficiently desulfurized.

Accordingly, it is required to provide a diesel fuel additive, particularly for diesel fuels of low sulfur content, that can reduce the production of deposits on fuel injection nozzles of compression-ignition diesel engines, improve the lubricity of diesel fuel, and further keep the fuel injection pump from wear.

The present invention resides in a diesel fuel additive comprising a salt of a carboxylic acid and an aliphatic amine, or an amide obtainable by dehydration-condensation between a carboxylic acid and an aliphatic amine.

The diesel fuel additive of the invention can be employed by blending into a diesel fuel, particularly, a diesel fuel of low sulfur content, in an amount of, generally, not more than 1 weight %, preferably 30 to 300 ppm.

Preferably, the carboxylic acid is represented by the formula:

$$R(COOH)_n$$

wherein R represents a hydrocarbyl group having 2 to 50 carbon atoms, and n represents an integer of 1 to 4. For example, the carboxylic acid may be a monocarboxylic acid having 8 to 30 carbon atoms, such as oleic acid.

The aliphatic amine may comprise a hydrocarbyl group having 2 to 50 carbon atoms and 1 to 10 amine nitrogen atoms. For example, the aliphatic amine may be a mono-amine which comprises a hydrocarbyl group having 8 to 20 carbon atoms. The aliphatic amine may be propylene diamine to which a hydrocarbyl group having 8 to 20 carbon atoms is attached. Specific examples are of aliphatic amines which may be used in the invention are oleyl amine and oleyl propylene diamine.

There are no specific limitations with respect to diesel fuel for which the invention is employable. However, the invention is preferably applied to diesel fuel, that is, a certain petroleum distillate, having a sulfur content of not more than 0.2 weight %, particularly not more than 0.05 weight %. Examples of the diesel fuels to which the invention is applicable, are those defined in JIS K 2204, Nos. 1 to 3, particularly, No. 3, which are treated to reduce the sulfur content to have the above content.

The salt of a carboxylic acid and an aliphatic amine and their amide which are employed as the diesel fuel additives in the invention are further described.

The salt of a carboxylic acid and an aliphatic amine can be obtained by mixing the carboxylic acid and the aliphatic amine at a temperature of 20 to 100°C. The amide can be obtained by subjecting a mixture of the carboxylic acid and the aliphatic amine to dehydration reaction at a temperature of 20 to 200°C under atmospheric or reduced pressure.

The carboxylic acid to be employed in the invention preferably is a compound which is represented by the formula:

$$R(COOH)_n$$

wherein R represents a hydrocarbyl group having 2 to 50 carbon atoms, and n represents an integer of 1 to 4.

The preferred hydrocarbyl groups are aliphatic groups such as an alkyl group and an alkenyl group, which may have a straight chain or a branched chain. Examples of preferred carboxylic acids are aliphatic acids having 8 to 30 carbon atoms and include capric acid, lauric acid, myristic acid, stearic acid, isostearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, caproleic acid, oleic acid, eraidic acid, linolic acid, linoleic acid, fatty acid of coconut oil, fatty acid of hardened fish oil, fatty acid of hardened rapeseed oil, fatty acid of hardened tallow oil, and fatty acid of hardened palm oil. The examples further include dodecenyl succinic acid and its anhydride.

The aliphatic amine preferably has a hydrocarbyl group of 2 to 50 carbon atoms in one molecule and amine nitrogen atoms of 1 to 10. Preferred are monoamines and diamines having a hydrocarbyl group of 8 to 20 carbon atoms. Their examples include coconut amine, capric amine, myristyl amine, stearyl amine, oleyl amine, tallow oil amine, stearyl propylene diamine, tallow oil diamine, and oleyl propylene diamine. Also employable are polyamines having a hydrocarbyl group of 5 to 50 carbon atoms such as ethylenediamine, diethylenetriamine, triethylene-tetramine, tetraethyl-enepentamine, and pentaethylene-hexamine.

The ratio of amount of the aliphatic amine to the carboxylic acid in the diesel fuel additive of the invention may be varied from 0.5 to 1.5 equivalents to one equivalent of the carboxylic acid. The diesel fuel additive may contain unreacted or unnuetrualized carboxylic acid or aliphatic amine within the range.

The additive of (1) the salt of carboxylic acid and aliphatic amine, or (2) the amide produced by dehydration-condensation of the carboxylic acid and aliphatic amine can be incorporated into diesel fuel in optionally adopted manner to prepare the diesel fuel composition of the invention. Two or more additives can be added to a diesel fuel separately or in admixture. The additive can be previously diluted with a small amount of a diluent oil such as kerosine, diesel fuel, or an aromatic solvent to give a concentrated additive solution and the concentrated additive solution can be incorporated into the diesel fuel to be treated. For instance, the diesel fuel additive of the invention can be mixed with a diluent to give a concentrated additive solution containing 1 to 70 weight percent of the diesel additive, and the thus obtained concentrated solution can then be diluted with the diesel fuel to be treated.

The incorporation of the additive of the invention, that is, the salt of carboxylic acid and aliphatic amine or the amide obtained therefrom, into diesel fuel in an amount of the specific range reduces the friction of the diesel fuel, keeps the diesel engine from wrong rotation, and obviates wear of the fuel injection pump. The amount of the diesel fuel additive of the invention generally is in the range of 10 ppm to 1 weight % of the diesel fuel, preferably 30 to 300 ppm.

The diesel fuel additive of the invention can be employed in combination with other diesel fuel additives such as low-temperature pour point depressant, cetane improver, anti-oxidants, metal deactivators, rust-inhibitors, corrosion inhibitors, demulsifiers and foam inhibitors, in the conventionally adopted amounts.

The present invention is further described by the following non-limiting examples.

(1) Preparation of Diesel Fuel Composition of Invention

1) Diesel fuels to be added

The two diesel fuels having the following characteristics were employed.

TAble 1

	Diesel fuel-A	Diesel fuel-B
Density (g/mL, 15°C)	0.837	0.831
Sulfur content (wt.%)	0.12	0.04
Distillation test (°C)		
Initial boiling	159	169
50% distillation	280	282
90% distillation	349	340
End point	356	366
Pour point (°C)	-12.5	-7.5
Dynamic vis. (mm^2/s, 30°C)	3.99	3.75

2) Diesel fuel additives

The following diesel fuel additives were prepared.

Additive-1: A salt of oleic acid and oleylamine in neutralizing equivalent amounts

Additive-2: A salt of one equivalent amount of oleylamine and 0.8 equivalent amount of oleic acid
Additive-3: A salt of oleylpropylenediamine and oleic acid in neutralizing equivalent amounts
Additive-4: An amide compound obtained by dehydration between oleic acid and oleylamine in neutralizing equivalent amounts under stirring at 120°C under reduced pressure

3) Preparation of diesel fuel compositions

The above mentioned diesel fuel additive was incorporated into the aforementioned diesel fuel to give the following diesel fuel composition.

Composition-1: prepared by incorporation of 50 ppm of Additive-1 into Diesel Fuel-A
Composition-2: prepared by incorporation of 70 ppm of Additive-1 into Diesel Fuel-A
Composition-3: prepared by incorporation of 100 ppm of Additive-1 into Diesel Fuel-A
Composition-4: prepared by incorporation of 150 ppm of Additive-1 into Diesel Fuel-A
Composition-5: prepared by incorporation of 100 ppm of Additive-2 into Diesel Fuel-A
Composition-6: prepared by incorporation of 100 ppm of Additive-3 into Diesel Fuel-A
Composition-7: prepared by incorporation of 100 ppm of Additive-4 into Diesel Fuel-A
Composition-8: prepared by incorporation of 100 ppm of Additive-1 into Diesel Fuel-B
Composition-9: prepared by incorporation of 100 ppm of Additive-2 into Diesel Fuel-B
Composition-10: prepared by incorporation of 100 ppm of Additive-3 into Diesel Fuel-B
Composition-11: prepared by incorporation of 100 ppm of Additive-4 into Diesel Fuel-B

(2) Evaluation of Lubricity

The diesel fuel compositions prepared as above were evaluated on their lubricity characteristics by the following HFRR test.

1) HFRR test

Coordinating European Council tentatively has determined HFRR Test (High Frequency Reciprocating Rig Test) in CEC-F-06-T94 as a standard for evaluating lubricity and anti-wear characteristic of a diesel fuel and diesel fuel additive which are designed to reduce wear of the fuel injection pump of diesel engine due to poor lubrication of diesel fuel.

According to HFRR test, a test piece is mounted on an electromagnetic vibrator which vibrates within a small amplitude. This test piece is pushed against another test piece which is fixed at its bottom portion. The friction and a diameter of wear area are then measured. The test temperature, frequency, amplitude of the vibration, and weight are optionally varied.

The evaluation of the diesel fuel additive of the invention was performed according to the method stipulated in CEC-F-06-T-94. The test temperature was 60°C.

Table 2

Test Sample	HFRR Test Result (60°C) Wear Diameter (mm)
Diesel Fuel-A (no additive)	0.54 (control)
Fuel Composition-1	0.48
Fuel Composition-2	0.44
Fuel Composition-3	0.41
Fuel Composition-4	0.36
Fuel Composition-5	0.39
Fuel Composition-6	0.41
Fuel Composition-7	0.43
Diesel Fuel-B (no additive)	0.56 (control)
Fuel Composition-8	0.44
Fuel Composition-9	0.40
Fuel Composition-10	0.45
Fuel Composition-11	0.45

The results set forth in Table 2 indicate that the fuel compositions 1 to 11 aii give reduced wear size and improve anti-wear characteristic.

(3) Evaluation of Detergency on Injection Nozzle

A flow rate through a new nozzle was measured using a flow meter set according to ISO 4010 before the following operation was started.

Nissan SD-22 engine (indirect injection type, nozzle type: throttle type, displacement: 2,164 cc) was run at a constant rate of an engine revolution of 4,000 r.p.m., torque of 50Nm for 6 hours. After the run was complete, the flow rate through the nozzle was measured by the above described method. The measured flow rate was compared with the flow rate measured on the new nozzle to evaluate the amount of deposit on the nozzle.

The results are set forth in Table 3.

Table 3

Test Sample	Decrease of Flow Rate (%) (at 0.1 mm lift)
Diesel Fuel-A (no additive)	73.8
Fuel Composition-3	58.4
Fuel Composition-5	55.3
Fuel Composition-6	57.6
Fuel Composition-7	59.8

The results set forth in Table 3 indicate that the diesel fuel composition containing the fuel additive of the invention is less than the diesel fuel containing no additive in the decrease of flow rate and hence improves detergency in the injection nozzle.

When the diesel fuel additive of the invention is incorporated into a diesel fuel, particularly a diesel fuel containing a less amount of sulfur, the additive is effective to reduce the amount of deposit in the injection nozzle of a diesel engine of a pressure ignition type, improve lubricity of the diesel fuel, and reduce wear of the fuel injection pump.

Claims

1. A diesel fuel additive comprising a salt of a carboxylic acid and an aliphatic amine, or an amide obtainable by dehydration-condensation between a carboxylic acid and an aliphatic amine.

2. The diesel fuel additive as defined in claim 1, wherein the carboxylic acid is represented by the formula:

$$R(COOH)_n$$

wherein R represents a hydrocarbyl group having 2 to 50 carbon atoms, and n represents an integer of 1 to 4.

3. The diesel fuel additive as defined in claim 1 or 2, wherein the carboxylic acid is a monocarboxylic acid having 8 to 30 carbon atoms.

4. The diesel fuel additive as defined in any one of claims 1 to 3, wherein the aliphatic amine comprises a hydrocarbyl group having 2 to 50 carbon atoms and 1 to 10 amine nitrogen atoms.

5. The diesel fuel additive as defined in any one of claims 1 to 4, wherein the aliphatic amine is a mono-amine which comprises a hydrocarbyl group having 8 to 20 carbon atoms.

6. The diesel fuel additive as defined in any one of claims 1 to 5, wherein the aliphatic amine is propylene diamine to which a hydrocarbyl group having 8 to 20 carbon atoms is attached.

7. The diesel fuel additive as defined in any one of claims 1 to 6, wherein the carboxylic acid is oleic acid.

8. The diesel fuel additive as defined in any one of claims 1 to 7, wherein the aliphatic amine is oleyl amine or oleyl propylene diamine.

9. A diesel fuel composition comprising a diesel fuel and a diesel fuel additive as claimed in any one of the preceding claims dissolved in the diesel fuel.

10. The diesel fuel composition as defined in claim 9, which comprises 1 to 70 weight % of the said diesel fuel additive.

11. The diesel fuel composition as defined in claim 9, which comprises 10 ppm to 1 weight % of the said diesel fuel additive.

12. The diesel fuel composition as defined in claim 9 or 11, wherein the diesel fuel contains not more than 0.1 weight % of sulfur.

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 2039

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 581 039 A (HORODYSKY) * the whole document *	1-4,6-12	C10L1/22 C10L1/18
X	WO 95 33805 A (EXXON) * page 9, line 21; claims 1-3,7-11,14-17 *	1,2,4,5, 8-12	
X	FR 2 426 730 A (EXXON) * page 14 - page 18; example 7 *	1-5,7-9, 11	
X	FR 2 403 381 A (COMPAGNIE D'EXPLOITATION DES PRODUITS INDUSTRIELS) * the whole document *	1-4,6, 9-11	
P,X	WO 96 23855 A (EXXON) * page 9, paragraph 2; claim 1 *	1-4,9-12	
X	US 2 805 135 A (BELL ET AL.) * the whole document *	1-4,7, 9-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	US 2 456 569 A (SMITH) * the whole document *	1-5,7-11	C10L
X	DE 28 52 541 A (B.V. BEVEROLFABRIEKEN) * page 6, line 1 - line 5 *	1-5,7,8	
X	EP 0 393 769 A (AGIP PETROLI) * the whole document *	1,2,9-11	
X	US 2 684 292 A (CARON ET AL.) * column 2, line 29 *	1,4,5, 8-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 May 1997	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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